Watershed Scale Simulation to Explain Observed Hydrogeochemical Trends and Mercury Bioaccumulation

Wes Rutelonis†, Mike Berndt‡, Chuck Regan•

† University of Minnesota – Department of Earth Sciences.

‡Minnesota Department of Natural Resources.

• Minnesota Pollution Control Agency.

Abstract

The Minnesota Department of Natural Resources and a number of other institutions have recently conducted studies that evaluate processes controlling the bioaccumulation of methylmercury in fish in the St. Louis River Watershed (SLRW). The role that sulfate impacted mine effluent plays in these processes has also been considered at great length. The results and syntheses of these investigations make available an array of physical data and scientific understanding that could be made significantly stronger by simulating interactive chemical and hydrological processes numerically. The State of Minnesota would undoubtedly benefit from the creation of a hydrological simulation program geared specifically to SLRWs' unique conditions and its already extensive body of research. Recent studies have generated a large database including flow measurements and water chemistry that can be used to calibrate and test conceptual models using relatively straight forward hydrologic simulation.

The initial modeling phase will include basic hydrologic budgeting at the watershed scale in order to determine the accuracy with which the hydrology of the model was calibrated. Adjustments will be made on an as needed basis. Once the hydrologic calibration has been tried and tested, its ability to characterize observed phenomenon in the watershed will be either confirmed or denied. If the model is indeed deemed useful at the watershed scale, it can then be used as a tool for demonstrating the relationships between important chemical constituents (ie. mercury, sulfate, iron and dissolved organic carbon). Supplementary experiments involving DOC cycling and the relative importance of hyporheic and riparian zones will be conducted to further constrain the models ability to replicate physical data. This projects major goal is to clarify the aforementioned geochemical relationships in order to assist in watershed planning with regards to pollution control.

Fish

Methylmercury in the St. Louis River Watershed is thought to be magnified up the food chain such that concentrations in fish tissues are often over a million times greater than the water they live in (Boudou and Ribeyre, 1997). Sulfate reducing bacteria in headwater sediment pores play an integral part in the methylation and eventual bioaccumulation of methylated mercury species in downstream predatory fish species.

Major Predatory Species

- Walleye (Sander vitreus, formerly Stizostedion vitreum)
- Northern Pike (Esox lucius)

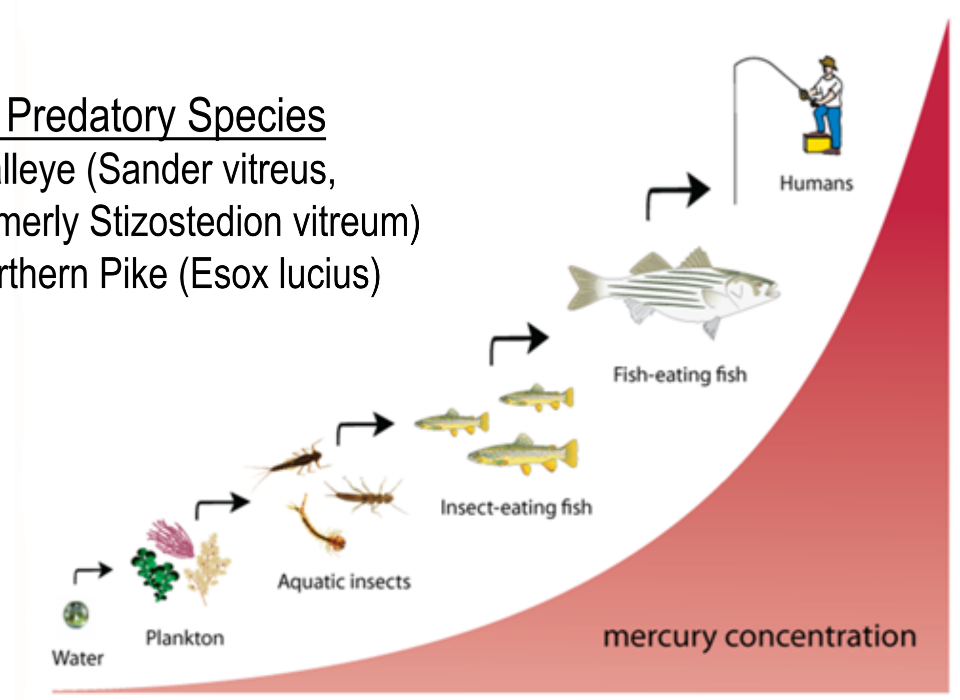


Figure 1: Trophic level mercury concentration distribution

Watershed

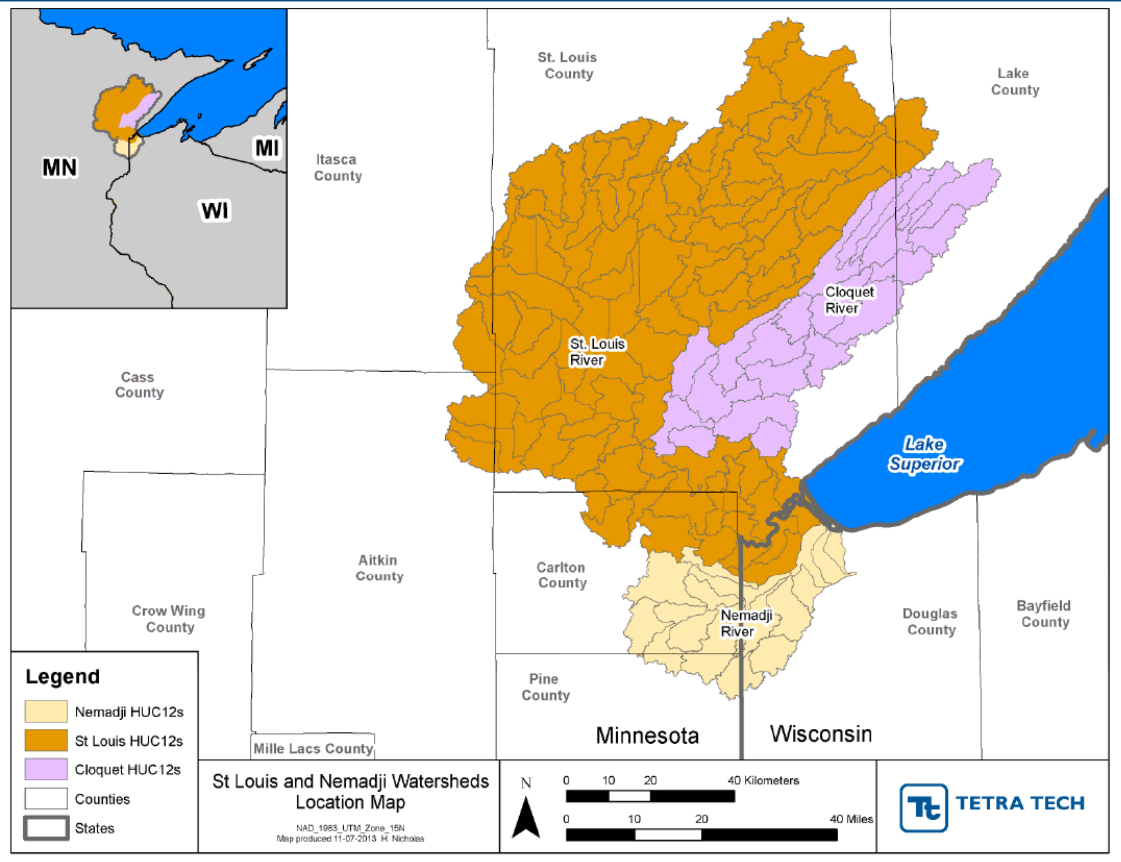


Figure 2: Watershed delineation. The St. Louis River Watershed is host to Mining operations while the Cloquet remains isolated from Mining input.

Background

The Biwabik Iron Range in Northern Minnesota hosts several taconite mining operations. The mining process generates large amounts of waste in the form of crushed rock. Due to its increased surface area, the crushed sulfide rock and the tailings basins that contain it are susceptible to high rates of oxidation and sulfate export. Much of the St. Louis River Watershed is impacted by elevated sulfate concentrations and the effect is still under review.

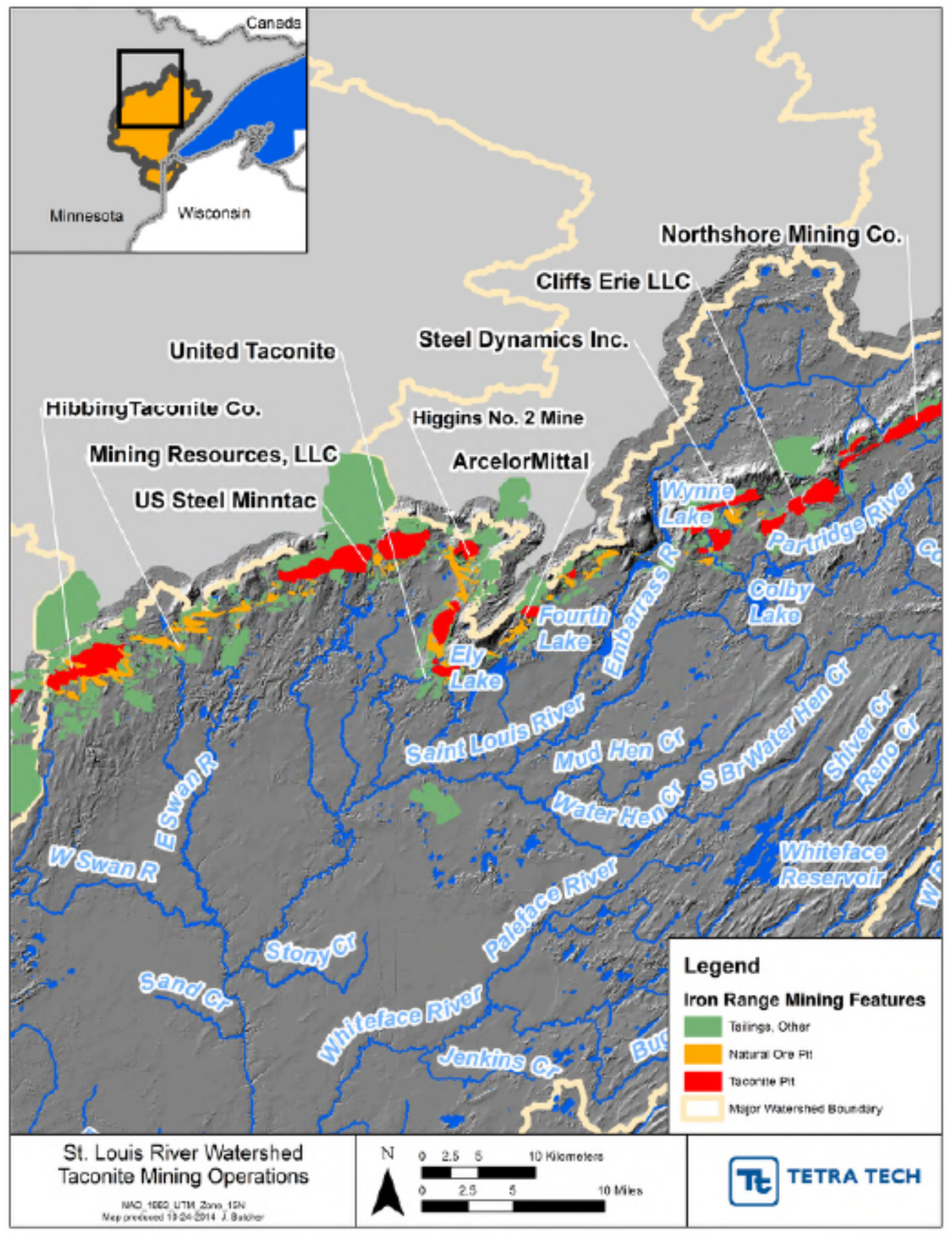


Figure 3: Biwabik Iron formation in the context of the St. Louis River Watershed

Modeling Phase I

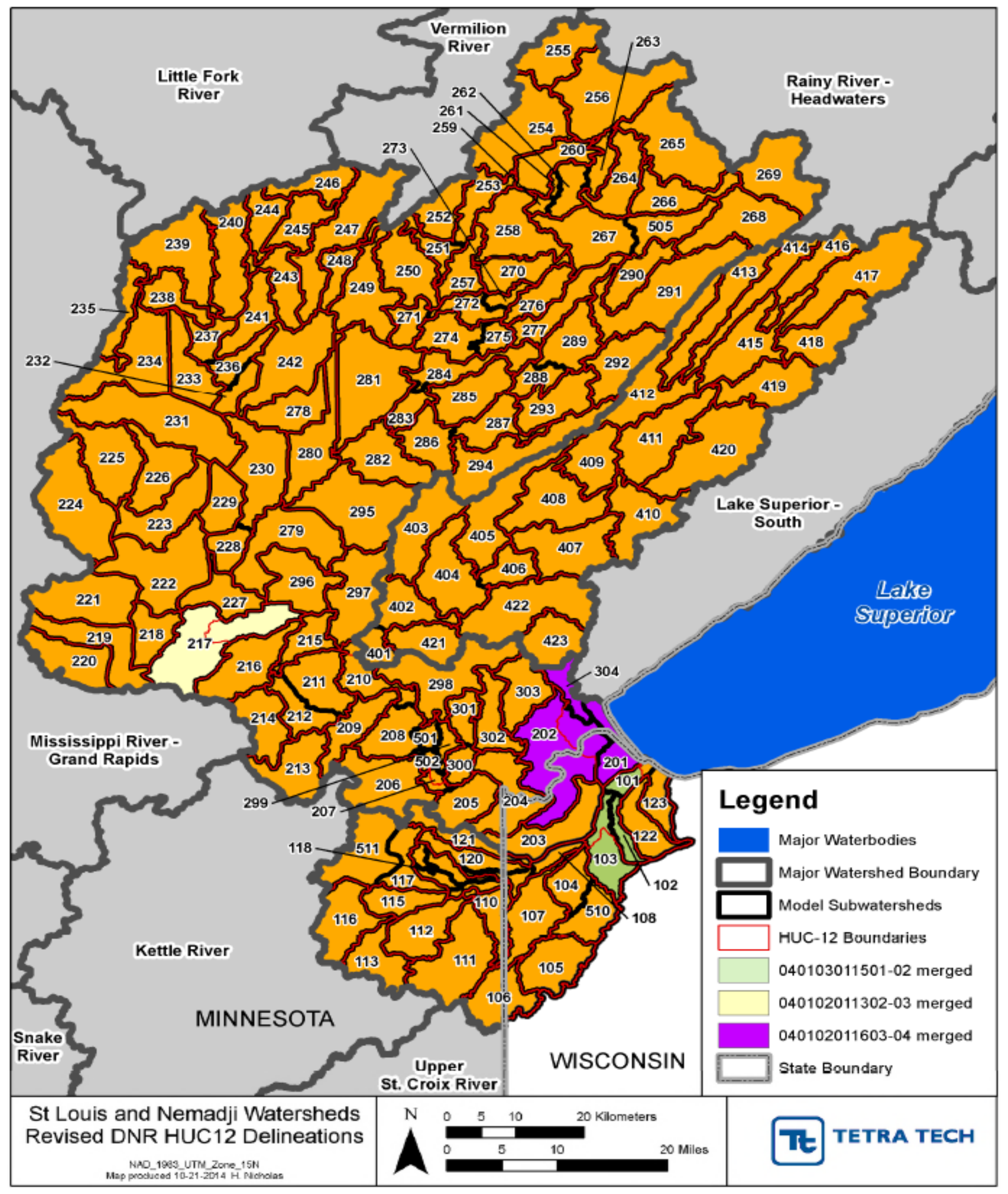


Figure 4: All three watersheds divided into subdelineations (HUC-12). Subdelineation allows for a more detailed glimpse into hydrogeologic controls and water budgets. This allows model users to analyze small and large portions of the watershed.

Dissolved Organic Carbon

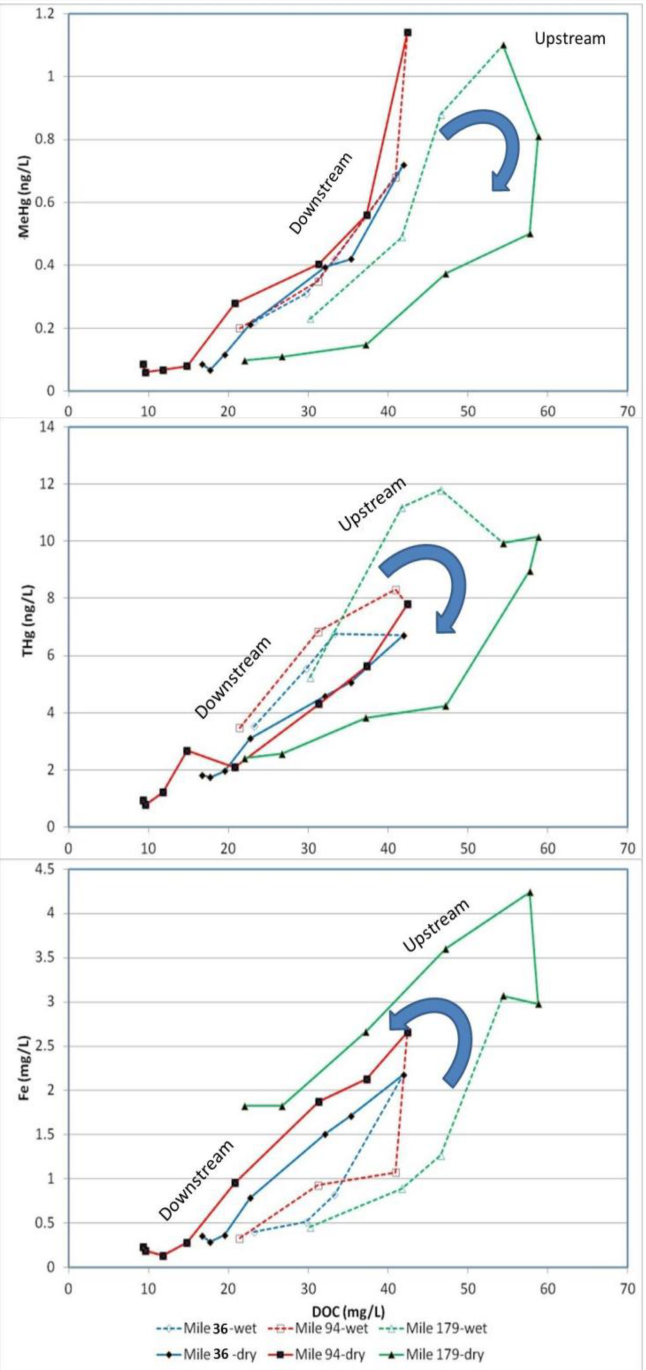


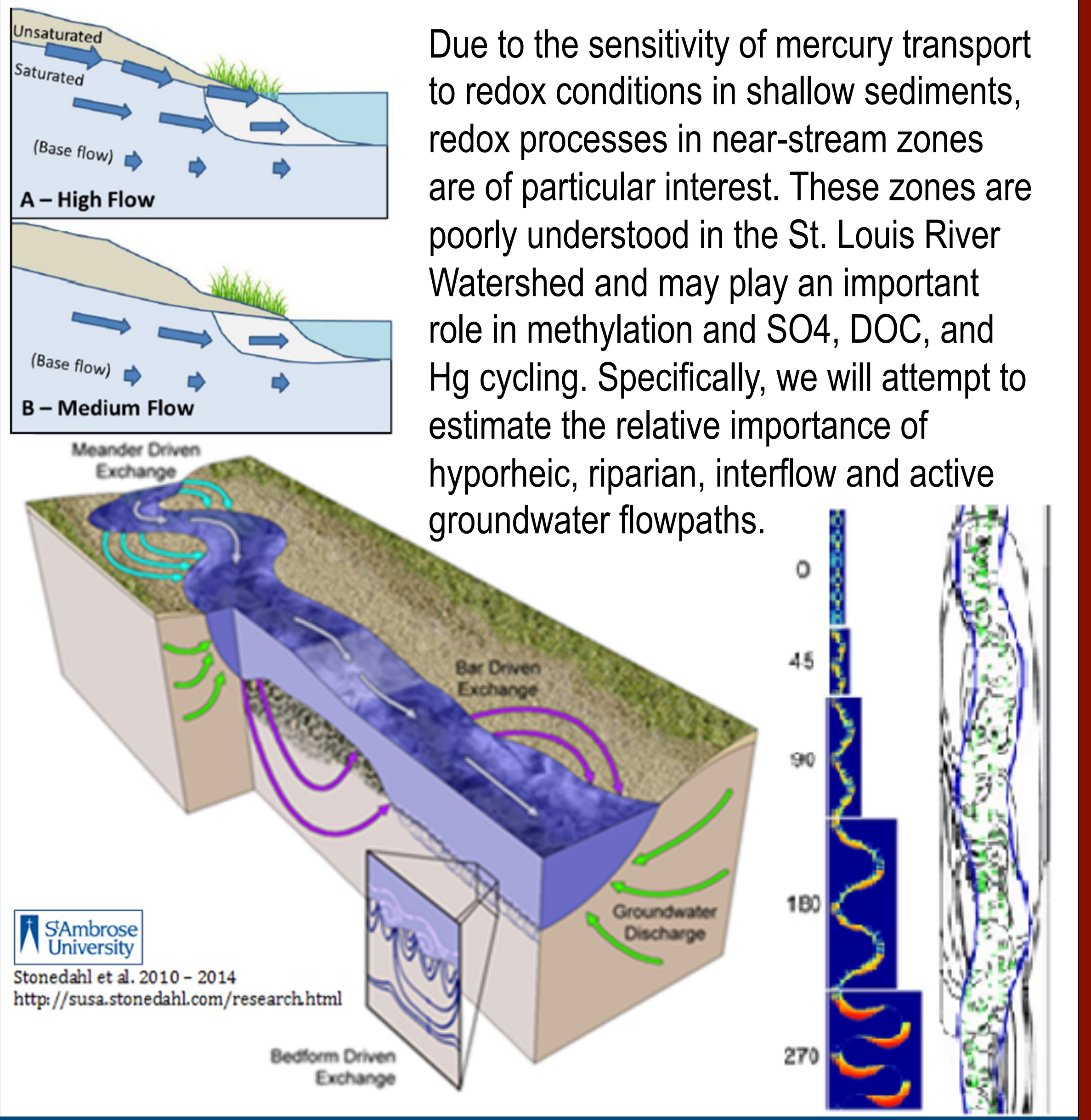
Figure4 shows an anomalous relationship between DOC and MeHg that suggests differing DOC behavior upstream from mining regions compared to downstream. During the transition from wet to dry, DOC in upstream waters increases while downstream (mine water impacted) does not change. This change in DOC did not, however, alter the MeHg concentrations in each portion of the watershed.

Observations throughout the watershed suggest that DOC may be behaving differently depending on the chemical makeup of the water. Sulfate levels from mining input in downstream waters may cause a low-MeHg component of DOC to flocculate out of solution which could explain the pictured trends.

Figure 4: DOC vs. Fe, THg and MeHg (Berndt, et al. 2014)

The United States Geological Survey has developed a technique for isolating particular DOC fractions from solution, extracting them and then freeze drying the resulting solid. Isolates are available for the St. Louis River that were collected during a high-flow period when DOC concentrations throughout the watershed were approaching their maximum values. One of these isolates (the most abundant form and one thought to control MeHg transport) will be carefully dissolved back into solutions containing both high and low SO4 concentrations.

Environmental Transport



Due to the sensitivity of mercury transport to redox conditions in shallow sediments, redox processes in near-stream zones are of particular interest. These zones are poorly understood in the St. Louis River Watershed and may play an important role in methylation and SO4, DOC, and Hg cycling. Specifically, we will attempt to estimate the relative importance of hyporheic, riparian, interflow and active groundwater flowpaths.

Acknowledgements

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Contact information

Office : 200K Pillsbury Hall

Email : rutel001@umn.edu

PI : Mike Berndt (MNDNR)